

This Page Is Inserted by IFW Operations
and is not a part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

IMAGES ARE BEST AVAILABLE COPY.

**As rescanning documents *will not* correct images,
please do not report the images to the
Image Problem Mailbox.**



Europäisches Patentamt
European Patent Office
Office européen des brevets

⑪ Publication number:

0 317 106
A2

⑫

EUROPEAN PATENT APPLICATION

㉑ Application number: 88310157.8

㉓ Int. Cl.: C08J 3/06 , C08J 3/24

㉒ Date of filing: 28.10.88

㉔ Priority: 29.10.87 JP 271798/87

㉕ Applicant: Nippon Shokubai Kagaku Kogyo Co., Ltd
1, 5-chome, Koralbashi Higashi-ku
Osaka-shi Osaka-fu 541(JP)

㉖ Date of publication of application:
24.05.89 Bulletin 89/21

㉗ Inventor: Nagasuna, Kinya
Hanada-shataku 11-55 4-65,
Higashisakayama-cho
Sakai-shi Osaka-fu(JP)
Inventor: Kadonaga, Kengi
1-1-12, Fukaehonmachi Higashinada-ku
Kobe-shi Hyogo-ken(JP)
Inventor: Kimura, Kazumasa
15-4, Yuhigaoka Sango-cho
Ikoma-gun Nara-ken(JP)
Inventor: Shimomura, Tadao
2-9-11, Shinsenrinishimachi
Toyonaka-shi Osaka-fu(JP)

㉘ Designated Contracting States:
BE CH DE ES FR GB IT LI NL SE

㉙ Representative: Myerscough, Philip Boyd et al
J.A.Kemp & Co. 14, South Square Gray's Inn
London, WC1R 8EJ(GB)

㉚ Method of surface-treating water-absorbent resin.

㉛ A method of treating the surface of a water-absorbent resin is disclosed which comprises adding a hydrophilic crosslinking agent capable of reacting with at least two functional groups of the water-absorbent resin in a hydrophobic organic solvent to crosslink resin at or near its surface. The hydrophilic crosslinking agent is added in the form of a dispersion which is obtained by dispersing it in a hydrophobic organic solvent in the presence of a surface-active agent.

EP 0 317 106 A2

a saturation concentration.

A conventional water-soluble radical polymerization initiator may be used in the polymerization. Examples include persulfates such as potassium persulfate, sodium persulfate and ammonium persulfate; hydroperoxides such as t-butyl hydroperoxide and cumene hydroperoxide; and azo compounds such as 5 2,2'-azobis-2-amidinopropane hydrochloride. Two or more of these polymerization initiators may be used in combination. Furthermore, redox systems composed of a combination of these polymerization initiators and reducing agents such as sulfites, L-ascorbic acid and ferric salts may also be used.

By the inverse-phase suspension polymerization method, the water-absorbent resin may be obtained by dispersing (suspending) an aqueous solution of a water-soluble ethylenically unsaturated monomer in an 10 inert hydrophobic organic solvent such as n-hexane, n-heptane, n-octane or cyclohexane using a dispersing agent such as a sorbitan fatty acid ester, a glycerol or polyglycerol fatty acid ester, a sucrose fatty acid ester, cellulose ether or cellulose ester, and then polymerizing the monomer in the presence of a crosslinking agent.

The method of this invention comprises adding a dispersion of the hydrophilic crosslinking agent 15 obtained by dispersing it in a hydrophobic organic solvent in the presence of a surface-active agent to a suspension of the water-absorbent resin obtained by dispersing it in a hydrophobic organic solvent, and then reacting the mixture to crosslink the surface and its vicinity of the water-absorbent resin.

The hydrophobic organic solvent used to suspend the water-absorbent resin may be any solvent which is inert to polymerization and other reactions. Examples include aliphatic hydrocarbons such as n-pentane, 20 n-hexane, n-heptane and n-octane; alicyclic hydrocarbons such as cyclohexane, methylcyclohexane, cyclooctane and decalin; aromatic hydrocarbons such as benzene, toluene and xylene; and halogenated hydrocarbons such as chlorobenzene, bromobenzene, carbon tetrachloride and 1,2-dichloroethane. Especially preferred are n-hexane, cyclohexane, chlorobenzene, toluene and xylene. If required, two or more of these solvents can be used in combination.

25 The amount of the hydrophobic organic solvent used is 0.4 to 20 parts by weight, preferably 0.7 to 10 parts by weight, per part by weight of the water-absorbent resin.

The hydrophilic crosslinking agent used in this invention may be any hydrophilic, preferably water-soluble, compound capable of reacting two or more functional groups of the water-absorbent resin. Examples include polyhydric alcohols such as ethylene glycol, diethylene glycol, triethylene glycol, 30 tetraethylene glycol, polyethylene glycol, glycerol, polyglycerol, propylene glycol, diethanolamine, triethanolamine, polyoxypropylene, oxyethylene oxypropylene block copolymer, pentaerythritol and sorbitol; polyglycidyl compounds such as ethylene glycol diglycidyl ether, polyethylene glycol diglycidyl ether, glycerol polyglycidyl ether, diglycerol polyglycidyl ether, polyglycerol polyglycidyl ether, sorbitol poly-glycidyl ether, pentaerythritol polyglycidyl ether, propylene glycol diglycidyl ether and polypropylene glycol 35 diglycidyl ether; polyvalent aziridines such as 2,2-bishydroxymethyl butanol-tris[3-(1-aziridinyl)propionate], 1,6-hexamethylene diisocyanate and diphenylmethane-bis-4,4'-N,N'-diethyleneurea; haloepoxy compounds such as epichlorohydrin and alpha-methylchlorohydrin; polyvalent aldehydes such as glutaraldehyde and glyoxal; polyamines such as ethylenediamine, diethylenetriamine, triethylenetetramine, tetraethylenepentamine, pentaethylenehexamine and polyethylenimine; polyisocyanates such as 2,4-toluylene diisocyanate, 40 and hexamethylene diisocyanate; polyvalent metal salts such as aluminum chloride, magnesium chloride, calcium chloride, aluminum sulfate, magnesium sulfate and calcium sulfate; and alkyl di(tri)halogenides such as 1,4-dibromobutane, 1,6-dibromoheptane and 1,3,5-trichloropentane. The polyhydric alcohol, polyglycidyl compounds, polyamines and polyvalent metal salts are especially preferred.

The suitable amount of the hydrophilic crosslinking agent used, which varies depending partly upon its 45 type, is generally 0.005 to 5 % by weight based on the water-absorbent resin. If it is less than 0.005 % by weight, no surface-treating effect can be obtained. If it is larger than 5 % by weight, the absorbancy of the resin may be reduced.

In the method of this invention, the addition of the hydrophilic crosslinking agent in the form of a dispersion obtained by finely dispersing it in the hydrophobic organic solvent in the presence of a surface-active agent is especially important for forming a uniform crosslinked layer on the surface of the water-absorbent resin and improving the various properties of the water-absorbent resin. In dispersing the hydrophilic crosslinking agent in the hydrophobic organic solvent, the hydrophilic crosslinking agent can be used as such or in the form of a solution in water or a hydrophilic organic solvent. Preferably, it is used as an aqueous solution for uniform dispersion.

55 The hydrophobic organic solvent used in obtaining the dispersion of the hydrophilic crosslinking agent may be the same as those used for suspending the water-absorbent resin. The amount of the hydrophobic organic solvent is 1 to 100 parts by weight, preferably 5 to 50 parts by weight, per part by weight of the hydrophilic crosslinking agent or its solution.

suspension of the polymer obtained in Example 5, and the mixture was stirred at room temperature. The mixture was heated to 75 °C and maintained at this temperature for 3 hours. The reaction mixture was filtered and dried as in Example 5 to give a comparative water-absorbent resin (2').

The properties of the comparative water-absorbent resin (2') were examined, and the results are shown in Table 2.

COMPARATIVE EXAMPLE 3

10

A solution of 0.03 g of tetraglycerol tetraglycidyl ether in 4 ml of water was added to the toluene suspension of the polymer below 28 mesh obtained in Example 7, and mixed with stirring at room temperature. The mixture was heated to 75 °C, and maintained at this temperature for 3 hours. Then, as in Example 7, the mixture was filtered and dried to give a comparative water-absorbent resin (3').

15

The properties of the comparative water-absorbent resin (3') were examined, and the results are shown in Table 2.

Table 2

20		Water-absorbent resin	Properties of the water-absorbent resin					
			Absorbancy (g/g)		Rate absorption (sec)	Drawing force (g)	Formation of an undissolved powder lump	
			3 minutes later	30 minutes later				
30	Example	1	(1)	43	57	40	16.4	No
		2	(2)	46	56	36	17.0	"
		3	(3)	45	58	34	16.7	"
		4	(4)	43	52	29	17.2	"
		5	(5)	41	58	29	17.6	"
		6	(6)	48	57	41	15.8	"
		7	(7)	38	51	35	16.3	"
35	Comparative Example	1	(1)	35	56	85	12.5	Yes
		2	(2)	31	52	60	13.0	"
		3	(3)	29	49	50	12.0	"

45 Claims

1. A method of treating the surface of a water-absorbent resin, which comprises adding a hydrophilic crosslinking agent capable of reacting with at least two functional groups of the water-absorbent resin to a suspension of the water-absorbent resin in a hydrophobic organic solvent to crosslink the resin at or near its surface, the hydrophilic crosslinking agent being added in the form of a dispersion obtained by dispersing it in a hydrophobic organic solvent in the presence of a surface-active agent.
2. A method according to claim 1 in which the surface-active agent comprises at least one nonionic, anionic, cationic or amphoteric surface-active agent.
3. A method according to claim 1 or 2 in which the dispersion of the hydrophilic crosslinking agent has an average liquid droplet size of 0.01 to 100 micrometers, preferably 0.01 to 50 micrometers.
4. A method according to any one of the preceding claims in which the hydrophilic crosslinking agent comprises at least one compound which is a polyhydric alcohol, polyglycidyl compound, polyamine, haloepoxy compound, polyvalent aldehyde or polyvalent metal compound.

5. A method according to any one of the preceding claims in which the hydrophilic crosslinking agent is used in an amount of 0.005 to 5% by weight based on the water-absorbent resin.
6. A method according to any one of the preceding claims wherein the hydrophobic organic solvent comprises at least one aliphatic, alicyclic, aromatic or halogenated hydrocarbon.
- 5 7. A method according to any one of the preceding claims in which the hydrophobic organic solvent used to suspend the water absorbent resin is used in an amount of 0.4 to 20, preferably 0.7 to 10, parts by weight based on the water-soluble resin.
8. A method according to any one of the preceding claims wherein the hydrophobic organic solvent used to obtain the dispersion of crosslinking agent is used in an amount of 1 to 100, preferably 5 to 50, parts by weight based on the hydrophilic crosslinking agent or its solution.
- 10 9. A method according to any one of the preceding claims wherein at least one of the at least two functional groups of the water-soluble resin is a carboxy, sulfonic acid or amino group.
- 10 10. A method according to any one of the preceding claims in which the water-absorbent resin has been obtained by subjecting an aqueous solution of a water-soluble ethylenically unsaturated monomer to inverse phase suspension polymerization in the presence of a crosslinking agent and a dispersing agent in a hydrophobic organic solvent inert to the polymerization.

20

25

30

35

40

45

50

55